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Project Summary

Vapor-Phase Cracking and Wet Oxidation as Potential Pollutant Control Techniques for Coal Gasification

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This research program was initiated with the overall objective of investigating the suitability of two techniques for pollutant control in coal gasification processes. These techniques are hydrocracking of heavy organics in the raw gas prior to quench, and wet oxidation of the gasifier condensate.

Experiments were carried out in bench-scale equipment to determine rates of hydrocracking and wet oxidation as a function of process conditions and the catalyst used. A microreactor system, capable of holding 1.0 cm^3 of material to be screened for catalytic activity, was used for the hydrocracking studies. Benzene and alkylated benzene compounds were used as model compounds in determining the potential of various materials as cracking catalysts. Thiophene was used as a model compound for catalyst poisoning studies. Cracking rates were determined for materials produced from bituminous and subbituminous coals and materials containing iron and nickel. Experiments were carried out at 300° to 800°C and approximately atmospheric pressure. It was found that the most promising material screened was a triply-promoted iron-oxide-based ammonia-synthesis catalyst. It had the greatest activity at temperatures of practical interest for a control device and showed more sulfur resistance than the other materials screened. However, the catalyst was poisoned by sulfur, and attempts to regenerate it by air oxidation were not successful.

Wet oxidation experiments were carried out in a 1-liter autoclave system using gasifier quench water and a 10,000 ppm phenol solution at 150° to 200°C. In several of the experiments, gasifier char was added to the autoclave system. It was found that no measurable oxidation took place at 150°C. However, substantial oxidation occurred at 200°C. Coal char was found to be approximately double the rate of wet oxidation in the phenol solution, but had no apparent effect on the rate of oxidation of the components in the gasifier quench water. The rates of oxidation measured in the experiments were found to be in the range which would make wet oxidation of gasifier condensate competitive with other control techniques.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

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Introduction

In coal gasification systems where the blast-coal contacting is countercurrent in nature, high loadings of undesirable, heavy organic compounds in the raw gas from the gasifier are common. Typically the raw gas is quenched, giving rise to an aqueous condensate stream which is characterized by a heavy organic loading and, in some instances, may contain emulsified tars and oils. Treatment of the aqueous condensate for reuse in the gasification process presents expensive and formidable problems to the widespread commercialization of coal gasification processes. For example, the cost of the equipment necessary for treatment of the condensate in a Lurgi high-Btu gasification plant represents a minimum of 8 percent of the total capital investment.

The processing steps used in condensate treatment include solvent extraction, biological oxidation, and adsorption. However, temperature and pressure conditions of the raw gas and condensate make two other processes look technically attractive for control of undesirable components. These processes are (1) vapor-phase cracking of undesirable components prior to quenching the raw gas, and (2) wet oxidation of the condensate.

Vapor-phase cracking could be carried out by placing a catalytic reactor between the gasifier and the quench system. However, an appropriate catalyst must be found that can withstand the severe conditions and poisons to which the catalyst would be subjected. Also, to be economically feasible, the cracking would have to take place at temperatures close to the outlet gas temperatures of the gasifier, or about 400° to 500°C. A successful vapor-phase cracking process would have advantages over the traditional quench-then-treat approach since eliminating heavy organics from the raw gas at high temperature would: reduce operational problems downstream of the gasifier, permit the recovery of high quality waste heat, and reduce the cost of condensate cleanup for reuse in the gasification process.

The other approach, wet oxidation, is a process in which dissolved or suspended organic material is oxidized in the liquid phase at an elevated temperature and partial pressure of oxygen. It is currently used as an industrial waste treatment method in a number of installations around the world. In gasification processes which utilize a shift converter, the desirable level of steam in the feed to the shift converter is on the order of 40 percent. In order to maintain this level, the quench system must be operated at 210° to 230°C and 600 to 1000 psig. These are ideal conditions at which to feed oxygen into the condensate and carry out wet oxidation of the organic material.

To investigate these control techniques, the Research Triangle Institute (RTI) has been carrying out an experimental program. Cracking studies were performed in small bench-scale equipment (microreactors). Based on previous studies in the literature, model aromatic and sulfur-containing compounds were selected and cracked over coal-derived materials, various metals, and commercial catalysts. In the wet oxidation experiments, phenol in water solutions and coal gasifier quench waters were oxidized in the presence of coal-derived materials. This report presents the results of these studies.

Conclusions

The results of the experimental studies on the cracking of selected aromatic compounds over coal-derived materials show that these materials can increase the rate of cracking of the aromatics by three orders of magnitude over the homogeneous vapor-phase rate. Gasification char produced from a subbituminous coal showed a greater enhancement of cracking rates than chars produced from bituminous coals.

Several iron- and nickel-containing materials were evaluated for activity toward enhancing hydrocracking of benzene (the most stable ring compound). It was found that an iron-oxide-based ammonia-synthesis catalyst completely hydrocracked benzene to methane at temperatures near 450°C, which is a temperature of practical interest for the Lurgi gasifier. However, the iron catalyst was found to be poisoned by sulfur compounds. Based on work in the literature on hot gas cleanup (sulfur removal) with iron oxide, regeneration of the poisoned iron-oxide catalyst may be possible. However, attempts made at RTI to regenerate the catalyst were unsuccessful.

The results from the experimental studies on wet oxidation of phenol-water solutions and gasifier quench waters showed that practical oxidation rates were obtainable. The presence of coal char in the wet oxidation system appeared to approximately double the rate of oxidation of the phenol, but had no effect on the rate of oxidation of the organic constituents in the gasifier quench water.

Based on the experimental studies, both vapor-phase cracking of heavy organics and wet oxidation of quench water appeared to have technical promise as control technologies in coal gasification processes. However, more information is needed in order to fully evaluate the technical and economical potential of the two control techniques.

Recommendations

Preliminary experimental results obtained on the cracking activity of an iron-oxide catalyst show it to be a promising hydrocracking catalyst in applications of controlling heavy organics in gasifier effluents. Catalysts composed of iron oxide are known to be regenerable from sulfur poisoning. Further work needs to be done in order to properly evaluate activation and regeneration steps for the catalyst and to investigate the effect of gas composition, pressure, temperature, and space velocity on the conversion of heavy organics in the presence of iron-oxide catalysts. Based on this information, actual tests in a coal gasification system should be planned and carried out in order to demonstrate the feasibility of cracking heavy tars in coal gasifier product gases. A preliminary economic analysis of vapor-phase cracking of undesirable components produced during coal gasification should be performed to establish the commercial potential of the control technique.

The work performed on wet oxidation of gasifier condensate and the use of coal char as an oxidation catalyst was a preliminary study and not planned to be exhaustive. Future work is needed so that a thorough technical and economic evaluation can be made of wet oxidation as a gasifier condensate and cleanup process. Experiments should be performed using (1) a wider and higher temperature range, (2) a range of oxygen partial pressures, (3) gasifier condensates with a wider range of CODs than used in this work, and (4) a variety of catalysts, including coal char or ash.

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The complete report, entitled "Vapor-Phase Cracking and Wet Oxidation as Potential Pollutant Control Techniques for Coal Gasification," (Order No. PB 81-219 594; Cost: $8.00, subject to change) will be available only from:
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